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Questions Concerning Environmental Mobility of Arsenic: Needs for a Chemical Data Base and Means for Speciation of Trace Organoarsenicals

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Biomethylation of metals, including arsenic, apparently occurs as a global process. Health control strategies therefore depend on accurate analysis of arsenic's environmental mobility. Determining to what extent biotransformations occur and how resultant organometal(loids) are sequestered in food chains requires sophistication beyond present-day total element determinations. Rather, active molecular forms of arsenic must be speciated for each environmental compartment, and it is necessary to quantify the dynamics of arsenic's mobility. Thus, new chemical facts are needed yielding rates of methylation or demethylation of arsenic; partition coefficients of organoarsenicals between air, water, and organic phases; and arsenic redox chemistry in polar media. NBS research in this context is reviewed with examples of recent results emphasizing speciation methodology. Topic areas discussed are: the nature of aquated methylarsenic species (NMR and laser-Raman spectroscopy); transport of methylarsenicals from aqueous media (gas chromatography–graphite furnace AA detection applied to metabolic Me_3As formation); and speciation of involatile organoarsenicals in aqueous media (demonstration of HPLC utilizing element-specific AA detection and appraisal of electrochemical detectors).

Introduction

Biotransformations of metalloids such as arsenic have been known for years, but only in recent times has the ubiquitous biomethylation of arsenic (*1*) and a number of other elements, including heavy metals (*2–4*), become apparent as a general environmental process (*5*). Clearly, anthropogenic inputs in inorganic materials can and do enhance such transformations, resulting in transport of volatile or lipid-soluble pollutants. Moreover, there is evidence (*6*) that even higher organisms, specifically man, can invoke elimination processes which involve formation of methylarsenic compounds. Consequently, certain critical questions must now be raised: to what extent or at what rate do these organometallic transformations occur and how are the resultant organometal(loid)s sequestered in food chains and ultimately in man? Answers to these problems are vital to developing environmental control strategies and they form the analytical bases for meaningful forecasting in environmental health (*7*).

Two essential ingredients are necessary for generating a useful analysis of arsenic's enviromental mobility and fate. The objectives of the NBS organoarsenic research program are derived from these considerations. First, we must reliably determine arsenic concentration patterns based on so-called "natural" distribution cycles, and compare these with respect to documented perturbations stemming from man's technological inputs. Much survey work has already been conducted to this end, but future efforts require a level of sophistication beyond total element determination. That is, the active molecular form of the element must be established in each significant environmental compartment. Second, we need to know considerably more than is presently understood regarding the dynamics of arsenic's mobility through ecosystems. Specifically, we need to generate a base of chemical facts affording, for example, conditions affecting rates of methylation or demethylation of arsenic, partition coefficients between aqueous and organic phases for various key arsenicals, or the redox chemistry of organoarsenic species present in biological media.

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Obtaining these data is a major undertaking for the relatively few researchers in the field of environmental organometallic chemistry. The situation is made still more complex because a balanced interdisciplinary approach is necessary which involves a number of other specialities, especially in the life sciences. Nonetheless, effective attack on current questions regarding the impact of arsenic on man will rely on timely inauguration of such multifaceted efforts.

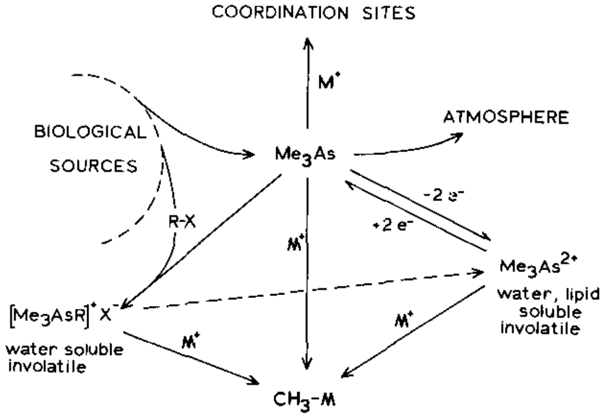


FIGURE 1. Transport of the known metabolite, trimethylarsine (Me_3As), from biotic sources with ultimate volatilization into the atmosphere must involve competition with a number of abiotic reactions: redox, demethylation, methylation, and coordination by other metals.

Approach

Background

Within its statuatory responsibilities relating to development and improvement of the national measurement system, the National Bureau of Standards provides a focus for technological, governmental and academic standardization for critical analyses of environmental materials. In recent years, NBS measurement advances, and production of Standard Reference Materials (SRM), increasingly have involved trace elements in natural or simulated environmental matrices (*8*). NBS also conducts an active conference and workshop program directed to continual assessment of current and future requirements in the environmental measurements field (*9*). All of these activities converge to provide an important contribution to the information base necessary to the development of a more comprehensive domestic and international environmental surveilliance program.

NBS Organoarsenic Effort

Based on the overall NBS mission and the clearly identifiable measurement problems in the arsenic field, the organoarsenic project conducted by the authors at NBS reflects both an interdisciplinary approach and a selective approach to this larger picture. The rudimentary arsenic cycle depicted in Figure 1 provides a pattern for describing the present effort and for reporting on current results.

Our earlier experiences with biomethylation (as well as reduction) of inorganic mercuric ion (*10*), as mediated by inorganic tin(IV) (*11*), coupled with more recent results obtained elsewhere describing biogenesis of methyllead (*12, 13*) or methylselenium (*14*), require caution be used in approaching questions of arsenic flux rates between environmental compartments, such as those involving sediment-water or water-air interfaces. As suggested by Figure 1, there is a likelihood that following exhalation of trimethylarsine (Me_3As) from a biological source or compartment, a number of significant competitive events may intervene to reduce or modify the form of vaporization of that gas into the atmosphere. Among these possibilities at least the following should be considered, based on current limited knowledge of arsenic's environmental chemistry.

(1) Dative-bond formation or complexation of Me_3As by electrophiles, such as transition metal cations, M (*15*) may occur. In some instances, such transition metal binding sites may themselves be of enzymatic importance to another biological process, thereby producing altered, possibly toxic, secondary effects in another organism (*16*).

(2) Metabolic Me_3As can interact with other natural products in the environment to produce new organoarsenicals of perhaps totally different toxicity. One process is that of quarternization of Me_3As by halocarbons RX (*17*) which are prevalent as metabolic MeBr or MeI from oceanic algae (*18*). This might represent an important long-term transport pathway for soluble but involatile ionic organoarsenic salts and explain the observed 1000-fold accumulation of arsenic in a species of marine kelp (*19*).

(3) The oxidation state of arsenic clearly plays an important role in its toxicity (*20*). Moreover, the

biomethylation process itself probably involves a series of reaction steps where both reduction and alkylation events are kinetically interdependent (*21*). The redox relationship between neutral Me_3As in aqueous medium and its stable water-soluble oxidized form $Me_3As^{+2}{}_{aq}$, probably constitutes a reasonable model for yielding quantitative measurements relevant to biological systems.

(4) Abiotic transmethylation between biologically active metal ions, M, has been demonstrated for several metals (*22,23*). Widespread availabilitv of methyl-, dimethyl-, or trimethylarsenic(III) or arsenic(V) species must be regarded as another important potential source for such transmethylation reactions, but as yet such chemistry in aqueous media has not received sufficient attention.

Recent NBS studies have sought to extend basic information concerning the formation and stability of methyl–arsenic bonds in aqueous media related to biological matrices. Coupled with this approach has been the concurrent effort to develop reliable, routine molecular characterization procedures, e.g., means for speciation, for such organoarsenicals at trace concentrations. This latter aspect must be regarded as intermediate to more sophisticated goals which seek to relate the abiotic chemical dynamics of organoarsenicals to their interactions with(in) biota in real environmental situations. A simple example would be the quantification of those factors controlling Me_3As flux from heavily polluted aquatic sediments as compared with pristine sediments.

Methodology

Inorganic reagents and organometallic compounds were obtained from commercial sources or synthesized by literature methods. Organic solvents used were of analytical or of spectraquality purity. All the organic arsenic, antimony, or tin compounds were authenticated by combinations of infrared and nuclear magnetic resonance (NMR) spectrometry (*23*), and elemental analysis. Air- and moisture-sensitive materials used in this work were manipulated under dry nitrogen, employing efficient recirculating dryboxes.

Weighed samples of compounds were obtained in the drybox and dissolved in oxygen-free distilled water saturated with nitrogen. Electrometric runs were conducted in deaerated $0.01M$ $NaClO_4$ aqueous solutions maintained under N_2 in closed vessels. Laser-Raman and NMR (proton) spectra were obtained on ca. $0.05M$ solutions of trimethylelement halides in water contained in capped 5-mm OD glass NMR tubes. For each of these solutions pH values were: Me_3SnBr, 2.75; Me_3SbBr_2, 1.55; Me_3AsBr_2, 1.51. Typically, both kinds of spectra were obtained within 24 hr after preparing the solutions.

Commercial instrumentation and operating conditions employed in obtaining the CW NMR spectra (*23*) and cyclic voltammograms (*24*) have been previously described. Laser-Raman spectra were obtained with a direct-recording grating spectrometer employing 514.5 nm light from a helium–argon laser (200 mW) collected at 90°C in a nonspinning cell with *f/*1 optics fitted with scrambler and polarizer. Special adaptation of a dual-beam atomic absorption spectrophotometer (AA) fitted with a graphite furnace atomizer (GFAA) permitted coupling directly to the effluent stream of a glass-column gas chromatograph (GC). The resulting GC–GFAA system provided appropriate direct molecular separation of volatile organoarsenical components, such as those volatilized by microorganisms, while giving continuous trace arsenic-specific detection of these separated gaseous components. Retention times for organoarsenicals were verified against authentic gases. Figure 2 illustrates GC–GFAA calibration curves and detection limits for several elements known to be biomethylated, in addition to As. Operational and performance details of the GC–GFAA system are described in another paper (*25*). Typically, for calibration curves dilute gas mixtures of the organometal in N_2 were injected directly into GC–GFAA in amounts of 0.05 to 2.0 ml.

The GFAA unit was also utilized in a conventional manner for batch (10 μl) solution analyses of eluant streams from a commercial high-pressure liquid chromatograph (HPLC) operating in a constant flow mode at 0.50 ml/min. By this simple expedient, detection of arsenic-containing (or some other metal) components separated on the HPLC column could be verified with considerable resolution, with variation only of flow rate of the mobile phase (here, *n*-heptane) and size of eluant fractions collected serially. Typically, in the demonstration given in this paper, two or three GFAA replicate analyses were performed on each fraction collected for 1 min, e.g., 0.5 ml of mobile phase eluted.

Mixed cultures of fungi present in the sediments of a pond on the NBS property in Gaithersburg, Maryland, were grown on Czapek-Dox medium (*26*) at ambient temperature (22°C). This substrate is favorable for growth of a wide variety of fungi. Cacodylic acid, $Me_2As(O)OH$ (200 ppm as As), was added to the basal medium along with necessary inorganic salts during preparation. Polycarbonate Petri dishes were used as culture vessels, following modification for direct sampling of head gases. A

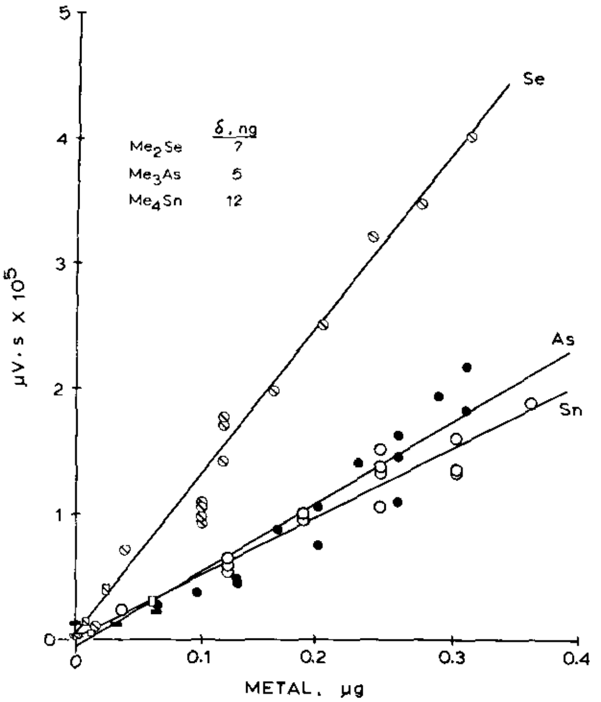


FIGURE 2. GC–GFAA calibration curves for (●) Me_3As, (⊗) Me_2Se, and (O) Me_4Sn are compared by using the appropriate wavelength for each element. Detection limits (δ) for each analyte (as ng element) are indicated for the graphite furnace operating at 1800°C in a Ar + H_2 carrier gas. Circles indicate single runs, rectangles signify five replicate runs.

line of 8–10 small holes (ca. 2 mm diameter) were melted across the top cover of each dish and closed with strips of Teflon tape held in place with clear plastic tape. One group of culture dishes was sealed with plastic tape to limit entry of atmospheric oxygen during growth; another group was placed in plastic bags which were periodically purged with pure O_2. Following periodic withdrawal of head gases (2.0 ml) samples from each Petri dish, the Teflon tape "septa" were immediately resealed with fresh tape. The syringed gas samples were injected directly into the GC–GFAA system without further manipulation and the AA outputs compared with current calibration curves.

Results and Discussion

Nature of Aquated Methylarsenic Species

We have earlier reported on the formation and chemistry of $Me_3As(V)$ and $Me_3Sb(V)$ species in protic solvents (*27*). In view of the oxidation of Me_3As (Fig. 1) by atmospheric oxygen, dissolved oxygen, or certain environmental metal ions, viz.,

$$Me_3As + Hg^{2+}_{aq} \rightarrow Me_3As^{2+}_{aq} + Hg^0 \qquad (1)$$

involvement of methylarsenic(V) intermediates must be regarded as potentially significant in arsenic transport. Unfortunately, comparatively little or no structural or kinetic data exists concerning the fate of Me_3As^{2+} in water, especially under conditions relevant to biological activity, e.g., pH 6–8, high salinity, and availability of many donor sites or ligands.

While several important properties of aquated methylarsenicals remain to be measured, we can draw inferences from our recent kinetic results obtained for closely related methyltin cations (*22, 23, 28*). Of interest are the important molecular rearrangements which occur upon hydration and hydrolysis, since such processes are critical to understanding molecular transport between air-water interfaces as well as the solution chemistry. Figure 3 illustrates an important case based on aquation (or, conversely, volatilization) of a trimethyltin halide.

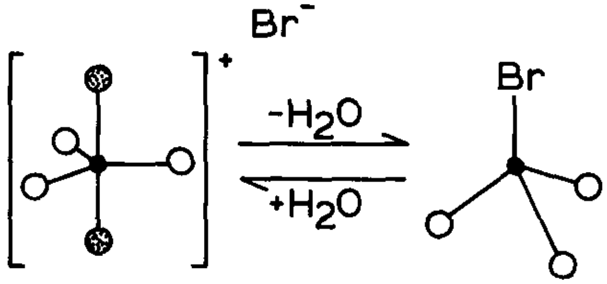


FIGURE 3. Molecular rearrangement can occur for an organometallic species during partition between a gas-water interface. This is equivalent to the hydrolysis of trimethyltin bromide (●) Sn; (O) CH_3; (⊗) H_2O.

In the gas phase, or in nonpolar solvents, this molecule assumes a nearly tetrahedral shape (C_{3v}), while in aqueous solution it rearranges to an ionic molecule with the three methyl groups convalently bound to the central tin atom in a symmetrical trigonal plane (D_{3h}) (*29*). Two equivalent axial water ligands can apparently complete the inner coordination sphere of the tin(IV) ion in certain cases (*30*). Should these ligands be neutral water molecules, the complete organotin ion bears a charge of +1; if solution conditions promote axial ligation by a charged OH^- or Cl^- ion, the methyltin species will carry a neutral or negative overall charge. The charge of the aquated organometal species is highly important to its subsequently methylation chemistry in reactions involving other metal ions. Moreover, evaluation of the organotin model is useful for defining the chemistry of methylarsenic(V) ions in water because: Me_3Sn^+ is isoelectronic with water-stable Me_3As^{2+} and Me_3Sn^+ shows a well-defined demethylation chemistry (*23*).

Trimethyltin cation (as well as its isostructural trimethyllead analog) is known to be a potent aqueous methylator, notably for inorganic Hg(II) ions,

$$Me_3Sn^+_{aq} + Hg^{2+}_{aq} \rightarrow Me_2Sn^{2+}_{aq} + MeHg^+_{aq} \qquad (2)$$

Such reactions can proceed quantitatively, but the rate of the process is highly dependent on salinity (pCl) *(23)* and total ionic strength μ of the reaction medium *(31)*,

$$\text{rate} = k_2[Me_3Sn^+][Hg^{2+}] \qquad (3)$$

which can cause k_2 to vary over 4–5 orders of magnitude (*23, 28*). Similar factors may be involved in demethylation reactions of arsenical ions. For example, if we imagine that in Figure 3 the central atom (•) is now arsenic and the bromine atom is oxygen (oxo- or $O^=$), it is seen that an isoelectronic derivative, Me_3AsO, can possibly interact on hydrolysis to form a trigonal pyramidal ionic species which is isostructural with the trimethyltin ion. Trimethylarsine oxide is probably one of the several oxo-arsenicals involved in environmental pathways. (*21, 27*).

$$\text{biota} \rightarrow Me_3As_g\uparrow \xrightarrow{\text{air}} Me_3AsO\downarrow \rightleftharpoons Me_3As^{2+}_{aq} \qquad (4)$$

the less volatile oxide being redeposited following intermediate transport by the metabolic Me_3As precursor. Although this possibility has not as yet been demonstrated, analytical and speciation capabilities now exist for its quantification (*32*).

Not only do similar considerations govern the transport properties of these and related polar organometallic molecules across air–water or lipid–water interfaces, it should also be recognized that partition coefficients appear to favor substantial concentration of the aquated organometallic ion in polar solvent phases (*33*). Evidently, fairly large heats of hydrolysis are associated with aquation of covalent molecules as exemplified in Figure 3 (*34*), but unfortunately neither such needed thermochemical data nor requisite partition coefficients have yet been reported in the literature (*35*). Consequently, quantification of reaction (4) must wait this additional experimentation.

In the present arsenic investigation, it was therefore desirable to initially establish the structural and ionic features of $Me_3As(V)$ species in water, thereby providing a reliable comparison with the established organotin reactions discussed above and forming an outline for future studies. Two nondestructive speciation methods were chosen for this preliminary work. These were nuclear magnetic resonance and laser-Raman spectrometry which could be readily employed in tandem on the same sample solutions.

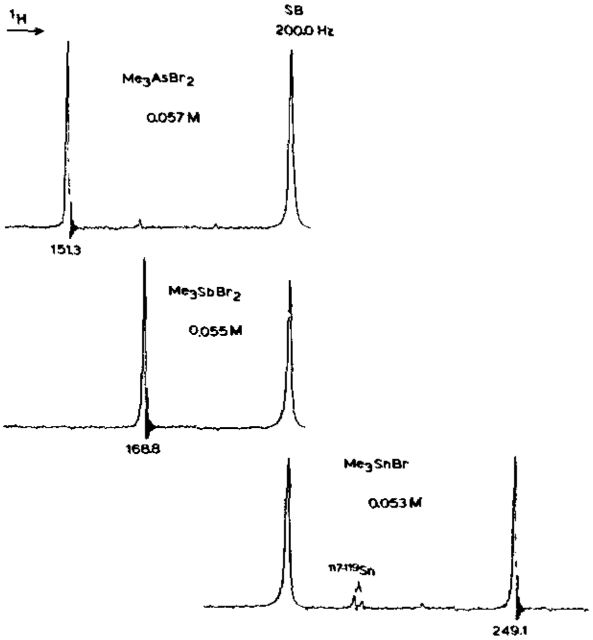


FIGURE 4. Proton NMR spectra obtained at *60 MHz (CW)* are compared for the methyl–metal(loid) ions indicated in 0.05*M* aqueous solution. The 200 Hz audio side band (SB) shown in each spectrum is one of several used to accurately measure the chemical shift of each methylmetal resonance. These values appear below each resonance in Hz upfield from the solvent water peak.

Proton NMR spectra of the highly acidic aqueous solutions of Me_3AsBr_2, Me_3SbBr_2, and Me_3SnBr are compared in Figure 4. Chemical shifts (in Hz) upfield from solvent water are consistent with the deshielding of methyl protons by the expected increasing electron-withdrawl by charged central metal(loid) atoms in the order: $As^{2+} > Sb^{2+} \gg Sn^+$. The single, sharp resonance peak observed for all the CH_3 protons bound to each ion results from either the three methyl groups being rigidly and symmetrically disposed about the central metal ion or a very rapid (on the NMR time scale) intramolecular reorganization process involving several configurations. A third possibility exists which involves rapid intermolecular exchange of CH_3 between metal centers. This process is held as unlikely inasmuch as the observed ^{117}Sn- or ^{119}Sn-proton spin coupling for Me_3Sn^+ or Me_2Sn^{2+} ions requires a stable CH_3-Sn bond. In addition, little or no hydrolysis of the methyl-metal bond itself (to produce CH_4 for example) is seen for any of these ions (*27, 33*).

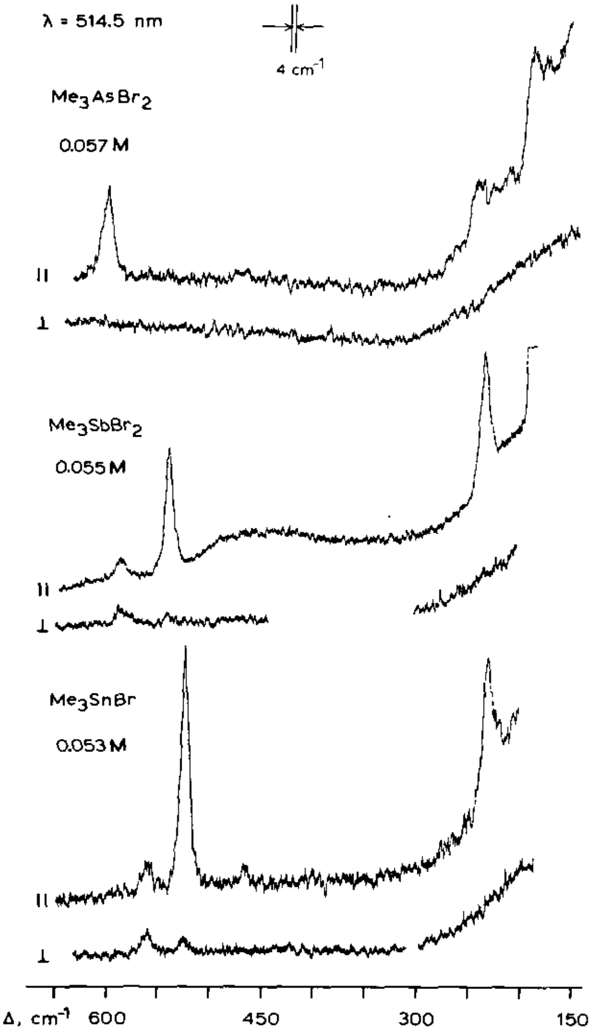


FIGURE 5. Laser-Raman spectra of the three NMR solutions of the methylmetal(loid) ions are compared by green light (514.5 nm) at moderate resolution (slit width = 4 cm^{-1}) and power (200 mW). Evaluation of polarized (∥) and cross-polarized (⊥) Raman scattering clearly demonstrate those molecular vibrations in the MC_3 skeletal region of 200-650 cm^{-1} which possess totally symmetric (a_1) properties.

The same NMR sample solutions were also examined by laser-Raman spectrometry which is a method particularly suited for optical spectrometry in aqueous media. This technique permits an appraisal of the symmetry of fundamental skeletal MC_3 molecular vibrations in a time scale (10^{-13}sec) much shorter than that afforded by NMR spectrometry (10^{-3} sec). Thus, it is possible effectively to "freeze out" the possible molecular motions noted before. In Figure 5 are partially depicted the results of our study on the three organometallic ions in polarized (∥) and depolarized (⊥) light. Each aqueous ion displays principal polarized absorption peaks as expected for symmetric a_1 Raman-active vibrations associated with trigonal skeletal modes (*33*). Figure 6 suggests the approximate molecular motions required for a trigonal bipyramidal (D_{3h}) structure which will satisfy these spectral symmetry properties, but we cannot presently exclude polarized Raman-active (a_1) bands similarly originating with a molecule of lower trigonal (C_{3v}) symmetry. For example, only a single ligand interaction (e.g., here, with OH_2, OH^-, or Br^-) can reduce the symmetry of the methyl–metal(loid) ion. The reorganization of the three methyl groups about the central atom in this $D_{3h} \rightarrow C_{3v}$ structural reorganization is, in effect, depicted in Figure 3 from the left to the right.

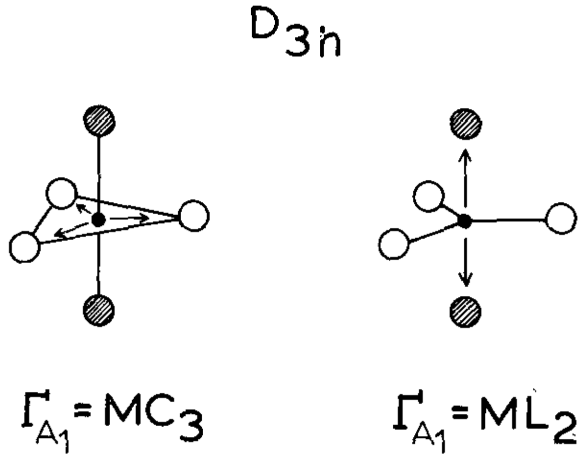


FIGURE 6. Totally symmetric Raman-active vibrations for the trigonal bipyramidal (point group = D_{3h}) molecule are approximately depicted: (●) As, Sb, or Sn; (○) CH_3; (▨) OH_2, Br^-, or OH^-.

These analytical considerations have practical relevance to extending our picture of aqueous methylarsenic chemistry, since such ligand interactions can both alter the net charge on $Me_3M^{n+}{}_{aq}$ ions as well as place new covalent bonds on the metal(loid). One or both of these effects may then significantly influence subsequent chemistry of the ions involved, but our prospects for perceiving such subtle diagnostic structural features for speciating such active intermediates are only at a beginning stage today. The long-known case of partial hydrolysis of trimethylarsenic(V) dihalides to produce isolable $Me_3As(OH)X$ compounds represents an important illustration (*36*). These hydroxyarsines form highly conducting aqueous solutions, but only limited infrared studies on anhydrous mulls have been reported (*36*).

Other workers have similarly examined the precursor Me_3MX_n compounds in various solutions by infrared or Raman spectrometry, including the Me_3SbX_2 system ($X = NO_3^-$ or ClO_4^-) and the Me_3SnX case ($X = Cl^-$ or Br^-). Their results, along with spectral data selected from other pertinent reports, are summarized in Table 1 along with the Raman results obtained in the present work. Common to all of the prior studies with aqueous solutions was the conclusion that no special features attributable to metal–halide or metal–oxygen (i.e., OH_2 or OH^-) vibrations were detectable. Earlier workers therefore concluded (*33,37*) that little or no covalent bonding exists between M^{n+} and X^- or OH^-, but rather only weak, highly polar coulombic interactions exist for these aquated species. As stated, Raman data are not yet available for the intermediate $Me_3As(OH)X$ compounds in aqueous solutions, but the infrared results suggest (*36*) that all five groups are covalently bound to arsenic(V) in the solid chloride material (trigonal bipyramidal structure), while the case for $Me_3As(OH)Br$ was regarded as inconclusive.

Table 1. Comparison of laser-Raman spectral frequencies for skeletal vibrations of aquated Me_3M^{n+} ions and covalent precursors.

Molecule^a	State	(Species) fundamental modes, cm^{-1}			Estimated point group	Reference
		(a_1) MC_3 stretch^b	(a_1) ML_n stretch	( ) Mc_3 deformation		
Me_3SnBr	Melt	512	219	(a_1+e) 148	C_{3v}	(*29*)
Me_3SnBr	H_2O	521	---	(e′) 152	D_{3h}	(*29*)
Me_3SnCl	H_2O	521	---	(e′) 152	D_{3h}	(*29*)
Me_3SnBr	H_2O	525P	232 P	---	D_{3h}	This work
Me_3SbBr_2	$CHCl_3$	514	164	(e′) 148	D_{3h}	(*38*)
Me_3SbX_2	H_2O	537P	---	(e′) 168 DP	D_{3h}	(*37*)
Me_3SbBr_2	H_2O	537P	234 P	---	C_{3v}	This work
Me_3AsCl_2	$CHCl_3$	563	260	(e′) 213	D_{3h}	(*39*)
Me_3AsBr_2	Solid	585	299	(a_1) 213	C_{3v}	(*39*)
Me_3AsBr_2	H_2O	602P	240 P	(a_1) 186P	C_{3v}	This work
$Me_3As(OH)Cl$	Mull^c	592	760^d 303^e	---	$\sim D_{3h}$	(*36*)
$Me_3As(OH)Br$	Mull^c	592	752^d ---^{e}	---	$\sim C_{3v}$	(*36*)
Me_3AsO	$CHCl_3$	588	875	(a_1) 224	C_{3v}	(*40*)

^{a}$X = NO_3^-$ or ClO_4^-.
^{b}L = ligand
^{c}Infrared spectra only.
^{d}As-O stretching
^{e}As-halide stretching
P = polarized band; DP = depolarized band.

On the basis of the present aqueous Raman data we assign the polarized (P) trigonally symmetric (a_1) MC_3 stretching vibrations as follows: $Me_3Sn^+_{aq}$, 525 cm^{-1}; $Me_3Sb^{2+}_{aq}$, 537 cm^{-1}; $Me_3As^{2+}_{aq}$, 602 cm^{-1}. These assignments are in good agreement with the earlier results listed in Table 1, but the interpretation of a symmetric (e.g., polarized) a_1 M-L stretching frequency is not straightforward. Although such bands were not previously detected for aquated Me_3SnBr or Me_3SbBr_2 species (*29, 37*), the additional lower frequency polarized bands observed in the present work (Fig. 5) below 250 cm^{-1} require presence of molecular vibrations also of a_1 type in either C_{3v} or D_{3h} structures. Thus for Me_3SnBr, the 232 cm^{-1} band can arise from either Sn—Br, Sn—OH or SN—OH_2 stretching vibrations. On the basis of the compound's known ionic behavior in water and the low pH (2.75) found for this solution (*23, 29, 33*) an initial hydration reaction appears more likely,

$$\underset{C_{3v}}{Me_3SnBr} + nH_2O \rightarrow \underset{\substack{C_{3v}\ (\text{if } n = 1)\\ D_{3h}\ (\text{if } n = 2)}}{[(H_2O)_n \text{---} SnMe_3]^+} + Br^- \tag{5a}$$

along with some partial hydrolysis to yield the observed acidic solution,

$$\underset{C_{3v}}{[(H_2O) \text{--} SnMe_3]^+} \rightarrow \underset{C_{3v}}{[HO\text{-}SnMe_3]^0} + H^+ \tag{5b}$$

Here, we assign (a_3) ν_{Sn-OH2} = 232 cm^{-1}, which implies a much weaker (more polar) bond than is seen (350–500 cm^{-1}) for several hydrated organometallic ions (*33, 41*).

The Me_3SbBr_2 case is interpreted as a similar hydration reaction,

$$\underset{D_{3h}}{Me_3SbBr_2} + H_2O \rightarrow \underset{C_{3v}}{[H_2O \text{---} SbMe_3Br]^+} + Br^- \tag{6a}$$

followed by more extensive hydrolysis (i.e., pH = 1.55) leading to the indicated changes in molecular structure as a monoacid,

$$\underset{C_{3v}}{[H_2O -- SbMe_3Br]^+} \rightarrow \underset{C_{3v}}{[HO\text{-}SbMe_3Br]^0} + H^+ \quad (6b)$$

In this instance, the polarized band at 234 cm^{-1} can arise either from (a_1) $\nu_{Sb-Br}\nu_{Sb-OH}$ or ν_{Sb-OH2} stretching modes, but this presently indeterminate.

It is clear why such well defined polarized ν_{m-L} bands should appear for these ions in the 0.05*M* solutions, whereas in the earlier reports (*29*, *37*) dealing with ca. 1–2*M* solutions of these ions no such absorptions are seen. Even in strongly basic solutions (6*M* NaOH), spectra of Me_3SnOH display no bands arising from Sn-O vibrations (*33*). Evidently, concentration effects can play a large role in the extent of hydrolysis and final pH of their solutions, and, consequently, the final net charge for such trimethyl-metal ions. Hydrolysis of Sb(V) as a diacid is not ruled out by present information, but is regarded as unlikely at low pH.

Applying the above considerations to the hydrolysis of Me_3AsBr_2 suggests a behavior similar to the antimony case. Based on the comparisons listed in Table 1, the two polarized bands observed at 240 and 186 cm^{-1} strongly support a C_{3v} structure following hydration, viz.,

$$\underset{C_{3v}}{Me_3AsBr_2} + H_2O \rightarrow \underset{C_{3v}}{[H_2O --- AsMe_3\,Br]^+} + Br^- \quad (7)$$

Either a weak H_2O--As or HO—As band or a weakened As-Br stretching mode gives rise to the higher absorption; based on previous work the last possibility is preferred. As a result, the Raman evidence implies Me_3AsBr_2 acts here as a monoacid to retain one As-Br bond upon hydrolysis to form a neutral $[HO\text{-}AsMe_3Br]^0$ species. Moreover, a symmetric a_1 AsC_3 deformation vibration is assigned to the lower band since no clearcut evidence was seen for a higher frequency ($\sim$ 750 cm^{-1}) a_1 As-O stretching band (*36*).

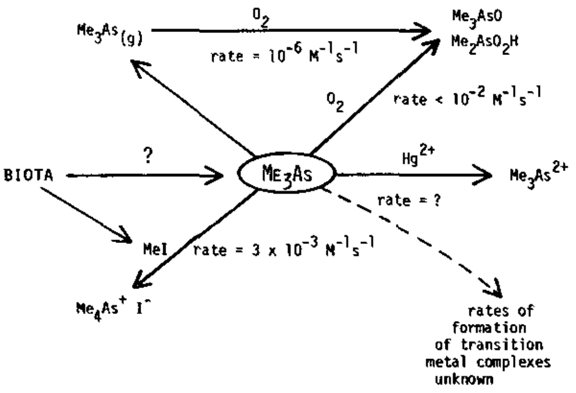
In view of the formation of "$Me_3As^{2+}{}_{aq}$" by reaction (1) with no evidence for demethylation of Me-As to form $MeHg^+$ as a competing product, we can draw a tentative inference from the foregoing Raman interpretations. In comparing the hydrolyzates of tin [reaction (5)] and arsenic [reaction (7)], it appears that the donor abilities of water are insufficient to fully displace all As-Br bonds while Me_3Sn^+ is fully aquated. Though both hydrates are of similar charge, the presence of halide on As will probably act as a more favorable nucleophile towards $Hg^{2+}{}_{aq}$ than will available methyl groups. In effect, the As-Br linkage acts as a blocking group inhibiting transmethylation. Other, polarizable or "good" ligands such as cyanide also effectively inhibit transmethylation between Me_3Sn^+ and Hg^{2+} (*22*), but the case for OH^- is unclear with the hydrolysates which involve a neutral species. Since there are described a variety of $Me_3As(OH)L$ compounds where L = NO_3^-, HSO_4^-, ClO_4^-, Br^-, Cl^-, etc. (*36*), a prospect exists for testing the importance in competitive situations of certain ligand substitutions or charge on methylation of Hg^{2+} by Me_3As^{2+} aquated species.

In general, we conclude that some partial ionic character obtains for all the hydrated $Me_3M^{n+}{}_{aq}$ species in dilute solutions where low pH values occur through partial hydrolysis. Additional spectral studies are now necessary, however, to resolve several important questions which can aid in future work on aquated methylarsenicals. In particular, the effects of very high and very dilute concentrations along with influences of pH changes (particularly more basic media), added ions (e.g., Br^-), and total ionic strength are called for. Use of D_2O as a solvent in joint NMR and laser-Raman spectral studies will be helpful. Here, the isotope effects of deuterated-bonds should assist in resolving the matters of weak DO--metal or D_2O---metal(loid) bonding, since detectable spectral changes could occur in O-H stretching modes for all the possibilities indicated in reactions (5)–(7) (*33*, *36*).

Tranport of Methylarsenicals From Aqueous Media

We have quantified the rates of several processes which can compete with the ultimate vaporization of biogenic Me_3As into the atmosphere (*17*, *27*). These values are summarized in Figure 7, where it can be seen that neither rates of oxidation by O_2 in aqueous solution ($k < 10^{-2}\ M^{-1}\ sec^{-1}$) nor methylation (quaternization) by MeI ($k = 3 \times 10^{-3}\ M^{-1}\ sec^{-1}$) significantly dominate. Indeed, it is anticipated that Me_3As which survives volatilization from aerated water will survive even much longer periods in air ($k = 10^{-6}\ M^{-1}\ sec^{-1}$). Nonetheless, substantial gaps in similar necessary data yet remain. For example, the partition coefficients for Me_3As between air and fresh or sea water are unknown. Although these quantities were recently reported for Me_2Hg (*42*), the residual dipolarity of the pyramidal (C_{3v}) Me_3As molecule and the availability of its lone pair of electrons for coordination suggest that inferences drawn from the isolated case with symmetric Me_2Hg may be misleading.

As previously stated, other reaction rates for redox of Me_3As are not available. Production of Me_3As^{2+} by Hg^{2+} reduction has not been measured, nor have kinetic studies been reported concerning



$Me_3As_{(g)}$
O_2
rate = 10^{-6} $M^{-1}s^{-1}$
Me_3AsO
Me_2AsO_2H
O_2
rate < 10^{-2} $M^{-1}s^{-1}$
BIOTA
?
Me_3As
Hg^{2+}
Me_3As^{2+}
rate = ?
MeI
rate = 3×10^{-3} $M^{-1}s^{-1}$
Me_4As^+ I^-
rates of formation of transition metal complexes unknown

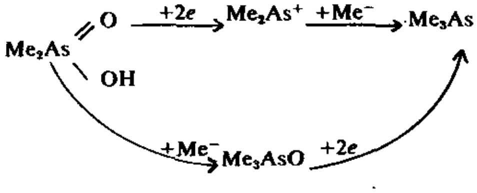
FIGURE 7. *Rates of several processes thought to be important in* the environmental mobility of arsenic are illustrated. A number of steps have not as yet been similarly quantified, including partition coefficients for organoarsenicals with water–air and lipid–water.

the formation of the lower methylarsenic (III) species in water, viz.,

$$As(V) \rightarrow As(III) \rightarrow MeAs^{2+} \rightarrow Me_2As^+ \rightarrow Me_3As\uparrow \quad (8)$$

Development of analytical methods for speciating these intermediates must be regarded as essential in view of the evidence that such species play a role in the methylcobalamin biosynthesis of dimethylarsine *(43)*.

Based on a consideration of reaction (4) and the rate data presented in Figure 7, we have conducted experiments which test possibilities for biogenic Me_3As release under both oxygen-limited and oxygen-rich atmospheres. While biomethylation of arsenic substrates has generally been regarded as favored under anaerobic conditions *(43)*, the results summarized in Figure 8 show that this is not necessarily the case. A mixed bacterial–fungal population cultured from a fresh water pond sediment can release free trimethylarsine under both aerobic and anoxic conditions. Here, pond microorganisms were grown on a favorable nutrient agar under a stress of 200 ppm of $Me_2As(V)$ (as As in cacodylic acid). Apparently, both the necessary reduction and methylation steps can occur in either $+O_2$ or $-O_2$ environments. Which step occurs first, if not both in concert, cannot be determined at this time, nor can the identity of principal As metabolites be made under the conditions employed, ranging from $-O_2$ to $+O_2$:



$$Me_2As(O)OH \xrightarrow{+2e} Me_2As^+ \xrightarrow{+Me^-} Me_3As\uparrow \quad (9a)$$

$$Me_2As(O)OH \xrightarrow{+Me^-} Me_3AsO \xrightarrow{+2e} Me_3As\uparrow \quad (9b)$$

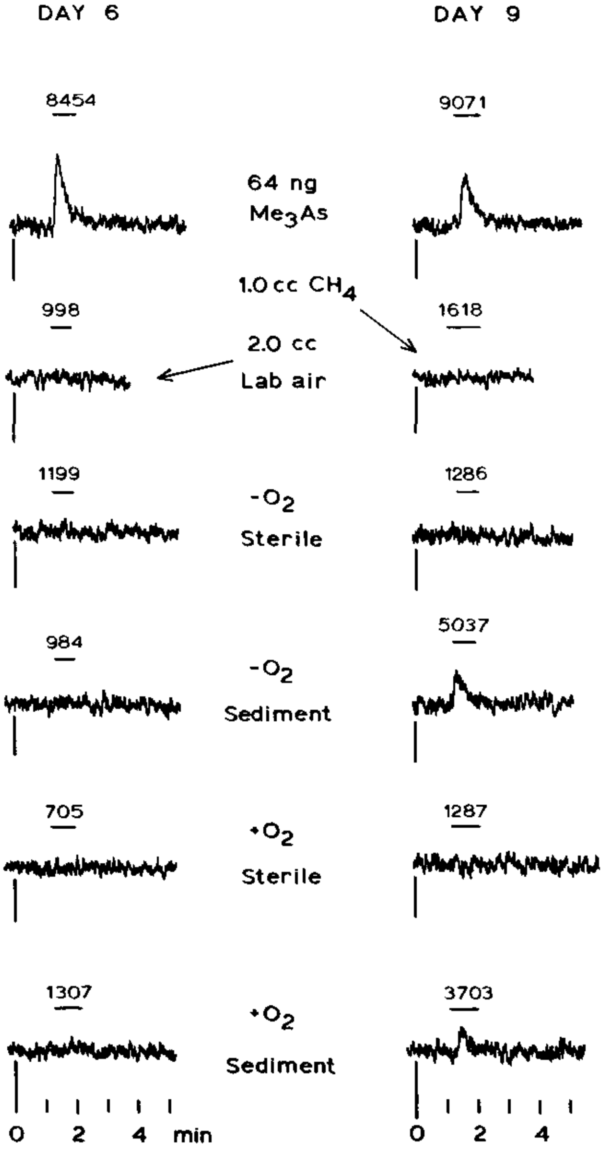


FIGURE 8. Using the GC–GFAA method, captive atmospheres above sterile controls and sediment inocula are compared with authentic Me_3As spikes (64 ng as As) and background laboratory air or CH_4. Both cultures grown under anoxic ($-O_2$) or oxygen-rich ($+O_2$) conditions show substantial production of gaseous Me_3As by 9 days, as resolved by its characteristic retention time of 93 sec, but no other arsine (*e.g.*, Me_2AsH) was detected. Horizontal bars above each chromatogram indicate the integration period (asμV-sec) covering the Me_3As retention region, with backgrounds typically at 800–1200. Not surprising is the appearance of less Me_3As in $+O_2$ conditions (3703) than that observed under reducing $-O_2$ conditions (5037).

It is probable that appropriate isotope labels can aid in similar future experiments, but a more desirable methodology will involve direct speciation of both the volatile biogenic arsenicals and those biomethylated products, such as Me_2As^+ or Me_3AsO which either form and remain in the growth medium or may be volatilized.

Speciation of Involatile Organoarsenicals in Aqueous Media

Much progress has been made in the past several years permitting speciation and quantification of volatile biogenic methylmetals (*9, 25, 32*). Underlying these methods has been the typical hydrophobic behavior of such covalent analytes and the consequent partition coefficients which favor their transport from solutions of origin into adjacent atmospheres. Analytical procedures basically dependent on sampling head gases have therefore proven effective. Among these methods, gas chromatographic separation and concentration serve admirably for isolation of metal-containing metabolites at growth concentrations, particularly when coupled with highly selective and sensitive element-specific detectors. The GC–GFAA system used in the present studies is one example of a method which permits direct detection and rate determinations of biogenic Me_3As in respirant atmospheres without any preconcentration or chemical conversions. Other related GC–metal detector schemes have also shown great utility in such investigations (*10, 25, 44–48*).

For a number of bioactive elements, particularly arsenic, biomethylation can result in formation of more complex, involatile products of variable oxidation state or coordination number. Unfortunately, many of these products may not be readily determined by vaporization methods. Braman and his co-workers (*44*) and others (*46*) have effectively utilized controlled reductive cleavage by hydrides as a pretreatment in order to generate simpler methylarsines, Me_nAsH_{3-n}. These volatile gases are then separated by low-temperature distillation and determined by an element-specific plasma spectrophotometer. This procedure and related extraction methods suffer in their use of destructive derivatization. For more complex lipido- or hydrophilic arsenic-containing metabolites possibilities for accurate molecular characterization are probably eliminated. Even for the simpler cases suggested by Figure 1 and reactions (4) or (8), severe hydridic reduction of mixtures in solution may not permit differentiation between Me_3AsO and $Me_3As^{2+}{}_{aq}$ or Me_3AsO and Me_3As, respectively. Certainly, for all such cases the reduction chemistry will need to be verified with authentic compounds if they are available.

In consequence, we have undertaken preliminary studies directed to applying liquid chromatographic (LC) procedures for speciation of trace quantities of organoarsenicals in polar media. Here again, the LC features a separation-concentration step on a carefully controlled column substrate followed by trace element-specific detection employing a conventional GFAA. The advantage of this approach lies mainly in its potential for reliable separation-concentration of trace amounts of involatile or sensitive organometallic molecules and ions in liquid phases under ambient and mild conditions. A very large range of solution or liquid sample conditions is compatible with the LC-GFAA method; analytes may be directly determined in organic solvents, electrolytes, or biotic fluids. Typically, useful molecular separations can be obtained at ambient temperatures through selection of column packing, mobile phase(s), and flow rate of eluants (*49*).

Heretofore, a limiting consideration in applying LC speciation techniques to trace organometallic analytes in polar media containing other complex organic metabolites has stemmed from restrictions of non-element-specific detectors. Commonly, LC or HPLC (high-pressure or "high-performance" LC) detectors utilize ultraviolet or visible absorption spectrophotometers operating at fixed wavelengths or a differential refractometer. Both approaches offer continuous monitoring of eluants but neither detector provides molecular or element-specific detection. For example, if an organoarsenical containing a phenyl moiety were present in a solution also containing other organic materials bearing aryl functions, a UV detector by itself could not assure the analyst that he had effectively separated and identified the phenylarsine from the other eluants bearing similar chromophores. On the other hand, some analytes, because they occur at very low concentrations or do not bear chromophores, may not be readily detected by the UV detector, if at all. In this case, we must turn to other more sophisticated schemes, among which element-specific detection is a preferable approach for trace speciation.

Figure 9 demonstrates application of the HPLC–GFAA system to an interesting situation common for commerical organometallic compounds produced in bulk. This was a sample of triphenylarsine reported to be 97% pure. The coincident detection by both a UV detector and the GFAA tuned at 193.7 nm for arsenic reveal that the compound is indeed impure, but that the impurities are organic in nature and do not contain arsenic. The "resolution" of the GFAA detector has not been optimized for this demonstration; that is, As determinations were performed on 2–3 10 μl sam-

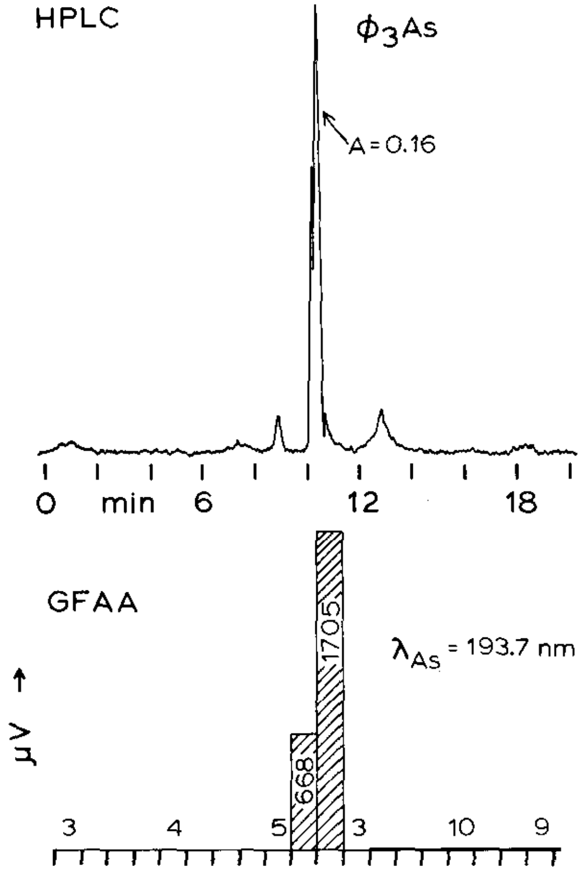


FIGURE 9. Conventional HPCL readout is displayed at top for a sample of commercial triphenylarsine $(C_6H_5)_3As$. Conditions were: column, Partisil 10; column temperature, ambient; mobile phase, *n*-heptane; flow rate 0.50 ml/min; pressure, 2300 psig; detector, UV at 254 nm; sensitivity 0.08 A full scale. Below are correlated the serial arsenic-specific GFAA analyses signals in μV corresponding to the above HPCL retention times or volumes. Representative low background levels (3–10μV) enumerated above several fractions show that the $(C_6H_5)_3As$ peak is clearly eluted after 10 min and that the other peaks seen in the UV tracing are not As-containing impurities. The spectra were obtained on ca. 1 μg As in 20 μl of *n*-heptane.

ples taken from each 500 μl batch of HPLC eluant stream acquired at 1-min intervals. This procedure can be improved in several ways. Assuming the LC conditions are optimal and that the same flow rate is desired (here, 0.5 ml/min), a simple automated fraction collector will permit ready stream analysis at 15-sec intervals. This is equivalent to a fourfold increase in the resolution depicted in Figure 9, but still provides adequate samples (125 μl) for replicate AA analyses. Alternatively, if a rapid qualitative survey is desired for evaluating retention times or presence of unknown arsenic-containing eluants, the size of the eluant sample fraction can be substantially increased without undue loss of As sensitivity.

Of particular note is the very desirable "sharpness" of the As-containing component and the very low background which preceeds and follows its elution. This result suggests that not only greater resolution can be achieved with smaller fractions of eluant, but that direct automation of the stream sampling can be realized with conventional "autosampling" equipment now commercially available for GFAA. Basically, all that is required is an automatic mechanical facility whereby periodic GFAA samples are withdrawn from a well into which the HPLC eluant stream continually flows. Requirements for sensitivity, resolution of metal-containing peaks, and flow conditions for optimal LC column performance will be major experimental factors. Such a facility is currently being evaluated at the NBS laboratory.

Two drawbacks should be noted in applying a GFAA detector for trace metal (e.g., arsenic) speciation of HPLC eluants. On the one hand, bulky AA instruments are costly, and on the other it is necessary to generate a "pulse" or interrupted dry-char-atomization sequence in order to achieve maximum element sensitivity (*32*). The GFAA detector therefore produces a noncontinuous readout of metal-containing species, but generally this offers no difficulties inasmuch as typical half-widths for well shaped LC chromatographic peaks can be easily regulated between 0.5 min and several minutes. We have selected the flameless atomic absorption mode as a best route to HPLC detection, mainly because of its inherently greater sensitivity towards most elements (metals) of interest (*32, 50*), and because it offers a reliable element detector which is comparatively little affected by solvent matrix effects. This last factor must be regarded as very significant for eventual application of HPLC–GFAA speciation to biotic fluids which contain substantial amounts of interfering solvated metal ions and chloride. Nonetheless, for the several faults indicated, we are also examining alternative LC detectors for organometals.

Recently, new and varied alternative LC detectors have been described in the literature. Some rely on electrometric (*51*) principles, others utilize chemiluminescent (*52*), electron spin resonance (*53*), and flame atomic absorption (*54*) detection schemes. Electrochemical detectors appear to offer many benefits; we are conducting preliminary studies on the electrochemical properties of a number of aquated organoarsenicals with the aim of developing relatively specific HPLC detectors. These would provide advantages of portability and low cost as a continuous readout detector which is capable of achieving very high sensitivity (pg range), albeit at the expense of element-specificity.

As suggested by the redox chemistry implicit in reactions (1) and (4) or (8), a number of the important methylarsenicals discussed in this paper may exhibit well-defined electroactivity. Myers et al. (*55*) earlier showed the utility of differential pulse polarography applied as a solution monitor for microbial transformations of arsenic oxidation states at ppm concentrations. Recently, additional reports have appeared which indicate favorable electroactivity for several important classes of organoarsenicals, viz., cacodylic and dimethylarsenic acids (*56*) [*cf.* reaction (9)], as well as triphenylarsine oxide (*57*).

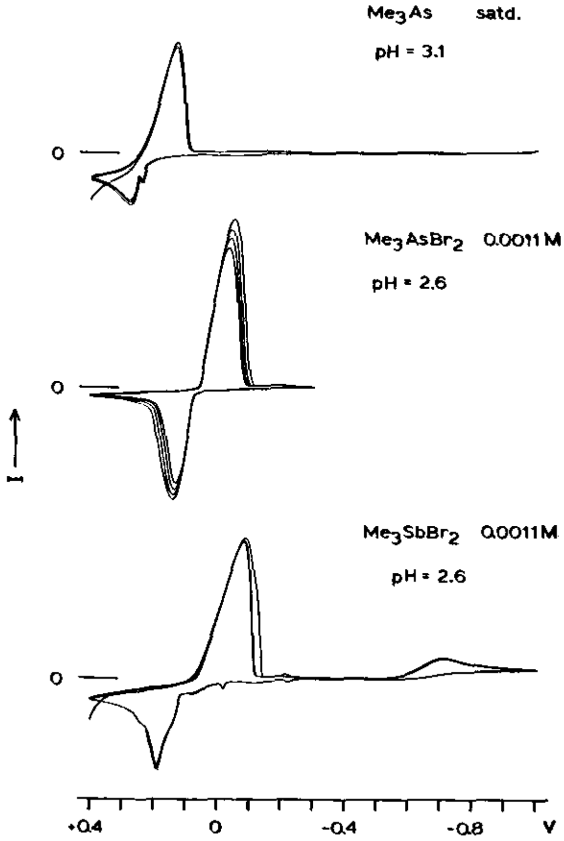


FIGURE 10. HMDE Cyclic voltammograms are compared for (*a*) Me_3As, (*b*) Me_3AsBr_2, and (*c*) Me_3SbBr_2 in 0.01*M* $NaClO_4$ aqueous electroyte. Operating conditions were: scan rates, 50 mV/sec (*b*, *c*) and 100 mV/sec (*a*); amplitude: 100 μA (*a*, *b*) and 200 μA (c) full scale.

A broad range of oxidative and reductive electrochemistry is apparently available for aquated organometallic species (*24*, *58*). Preliminary qualitative results are illustrated in Figure 10 for several of the methylarsenicals and related antimony compounds discussed in this paper. In general, very reproducible cyclic voltammograms of the type shown are produced at the low pH values cited, and these results indicate that both oxidative and reductive processes can be easily effected. In Table 2 are listed some of the preliminary redox data which suggest that well-separated potentials are available for flexible detector design and analyte specificity. Efforts in this area will continue to elucidate the mechanisms or organometallic electrochemistry because of its relevance to characterizing environmental redox processes. Emphasis, however, will be placed on optimizing eluant compositions and detector cell conditions in order to achieve optimum sensitivity (~ppb) for various HPLC applications. Careful choice of operating potentials, or even programmed changes in detector potentials while taking chromatograms, will offer improved sensitivity and selectivity for speciation of aquatic arsenicals (*59*).

Table 2. Organometallic redox processes in water as indicated by cyclic voltammetry.

Molecule	Oxidation, V[a]	Reduction, V[a]	Comments
Me_3As	+0.28	+0.14	
Me_3As^{2+}	+0.14	−0.04	
Me_3Sb^+	+0.02	−0.19	
		−1.66	Irreversible reaction
Me_3Sb^{2+}	+0.19	−0.08	
		−0.71	Complex oxidation
$MeHg^{+}$[b]	−0.50	−0.38	
		−0.55	Analytical peak
		−1.32	
		−1.22	Kinetic dependence

[a] V versus SCE.
[b] Data of Durst et al. (*24*).

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